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Electroluminescent Diodes from a
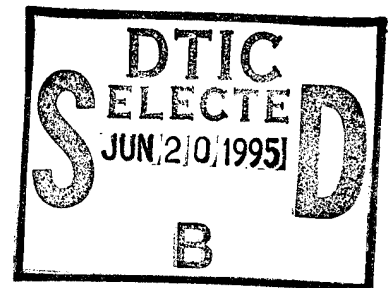Single-Component Emitting Layer of Dendritic Macromolecules

by

P. Wang, Y. Liu, C. Devadoss, P. Bharathi, and J. Moore

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13. ABSTRACT (Maximum 200 words)

Electroluminescent devices have been constructed using luminescent dendritic materials as the organic emitting layer. These dendritic macromolecules consisted of triphenylamines as the hole trapping groups, phenylacetylene segments for energy transfer, and 9,10-bis(phenylethynyl)-anthracene as the luminophor. These highly ordered, three-dimensional, covalent structures allow a modular approach to the design and construction of electroluminescent materials. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) indicated that dendrimers of generation greater than 3 formed uniform, crack-free films of thickness 600 ~ 1200 Å. Incorporation of triphenylamine units as hole trapping groups in dendrimer **2b** increased the current density and lowered the turn on voltage as compared with its hydrocarbon analog **1c**. Efficient energy transfer from phenylacetylene segments to the anthracene core is demonstrated by spectroscopic studies (absorption, emission, and excitation spectra). In the forward bias, these light emitting diodes (LEDs) radiate dim orange light .

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Electroluminescent Diodes from a Single-Component Emitting Layer of Dendritic Macromolecules

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The design and fabrication of efficient light emitting diodes (LEDs) based on organic materials has been an active area of research due to their possible applications in large area display technology. Organic-based devices have many potential advantages over conventional inorganic LEDs including their ease of fabrication, flexibility, low operating voltage and the ability to tune the color of the emitted light. Even though electroluminescence (EL) in anthracene single crystals has been known for over three decades,[1] that system suffers from major drawbacks like poor stability and high operating voltage. There was a sudden surge in this research field when Tang et al.[2] reported EL from thin layer of the aluminum chelate complex, 8-hydroxyquinoline aluminum. These devices were composed of a transparent ITO (indium tin oxide) layer which serves as the anode, an electroactive semiconducting organic layer, a coating of hole transporting layer (HTL, normally tertiary amines), and a layer of a metal with low work function as the cathode. The basic mechanism of these devices involves injection of holes from the anode (ITO), injection of electrons from the cathode (Ca, Mg or Ag), followed by recombination of these charge carriers in the organic emitting layer to generate excited states which emit light.

To improve the efficiency of these devices, an additional electron transporting layer (ETL) was added which increases the probability of radiative recombination. Adachi and coworkers[3] constructed three-layer devices (ETL/emitter/HTL) from various amines and found improvement in the EL efficiency. They were also able to observe blue emission from these devices. Interest in the organic LEDs intensified when Friend et al.[4] at Cambridge University reported the observation of EL from devices based on conjugated polymers (PPV and its homologues). Besides these two main categories of organic based LEDs, namely, one based on vacuum-deposited small organic thin layers and another on spin-coated polymers, there are recent reports of organic-inorganic heterostructure EL devices.[5]

Despite the enormous developments in this field, the quantum efficiency of organic LEDs remains very low. The highest internal efficiency achieved so far is 4% in PPV-cyanoPPV bilayer device made by Friend and coworkers.[6] The same group also fabricated a device from the copolymer PPV-DMeOPPV (Dimethoxy PPV)[7] in a single active layer which also had comparable efficiency. Further improvements are likely with even better defined systems.

Given the shortcomings with present EL materials, it is of interest to develop materials with improved efficiency, stability and that combine the advantages of small-molecule and polymer emitters. In this regard, dendritic macromolecules offer a special opportunity because they possess ordered, covalent three-dimensional structures which permit spatial control of active components and thus the electroluminescent properties of materials.[8] So far there has been no report of dendrimers being used as active luminophores in LEDs. However, Shirota and coworkers[9] have used "starburst" amine derivatives as effective hole transporting layers in some devices.

In this paper we report the fabrication of LEDs using new luminescent phenylacetylene dendrimers. These dendrimers can be viewed as modular luminescent materials consisting of a highly fluorescent core, 9,10-bis(phenylethynyl)-anthracene (solution $\phi_{fl} \sim 0.7$), a phenylacetylene monodendron for electron capture, and triphenylamine periphery to promote efficient hole transport and recombination (Scheme 1). Previous studies,[10] have indicated that the phenylacetylene monodendrons are capable of convergent and directed transduction of this excitation energy to the focal point luminophor. Thus, if charge recombination occurs in the dendritic segment, energy transfer to the luminescent core is expected. The dendritic architecture may help improve film quality because their globular structure provides low intermolecular cohesive forces leading to stable amorphous phases.[11] This should improve the stability of devices as gradual crystallization of the active material seems to be a main cause for the degradation of organic LEDs. In summary, assembling these components into a single

macromolecule can potentially enhance electroluminescence efficiency and simplify the device fabrication.

The luminescent dendrimers **1a-c** and **2a-b** shown in Scheme 2 were synthesized from 9,10-bis(trimethylsilylethynyl)-anthracene[12a] (1 equiv) and the corresponding phenylacetylene monodendron[12b] (2.1 equiv) by palladium catalyzed cross-coupling in the presence of K_2CO_3 and methanol.[12c] Due to the low stability of the core (9,10-bis(ethynyl)-anthracene), the deprotection and the coupling reaction were carried out in one step. The resulting mixtures were heated at 55°C under N_2 for 24 h or longer, and the products purified by flash column chromatography. The compounds were characterized by MALDI-TOF mass spectrometry, NMR, and GPC and confirmed to be homogeneous, monodisperse substances.
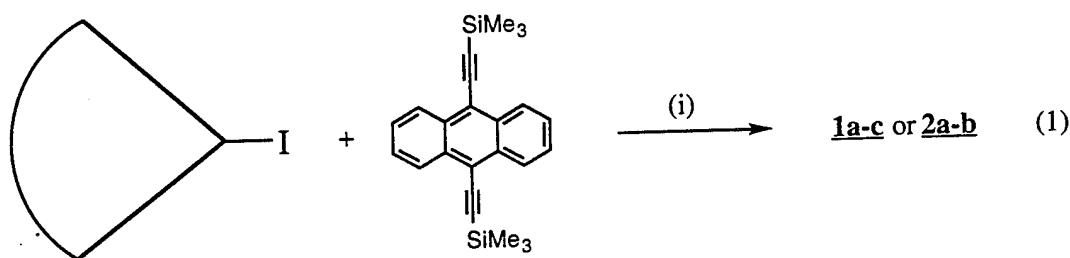
(i): Pd(dba)$_2$ (0.04 equiv.), PPh$_3$ (0.2 equiv.), CuI (0.04 equiv.), K_2CO_3 (0.01 equiv.), Et$_3$N/MeOH (3:1), 55° C, 24hr.

Electroluminescent diodes (LEDs) consisted of ITO coated glass which serves as the hole injecting electrode, a thin film of the dendrimer, and Mg/Ag alloy or Al as the electron injecting electrode.[13] A uniform thin film of dendrimers on the ITO surface was obtained by spin-casting a THF solution containing **1c** (1%), or **2b** (1%) at a spin rate of 2000 rpm. Crack-free, conformal thin films were obtained from generations **1c** and **2b**. Lower generation dendrimers gave films of inferior quality. The film thickness (measured by a Daktak stylus profilometer) for the dendrimers **1c** and **2b** was 1200, and 600 Å, respectively. The film quality was examined by scanning electron microscopy

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(SEM) and X-ray photoelectron spectroscopy (XPS). Both techniques suggested that uniform and crack-free films without pinholes were obtained. The electron injecting electrode (Mg/Ag or Al) was deposited on top of the polymer film by vacuum deposition at a pressure below 3×10^{-6} Torr, yielding a metal layer having a thickness of 2000 Å over an area of 0.08 cm^2. The contacts between electrodes and external wires were provided by silver paint. Electrical measurements were performed on a Keithley 617 electrometer. Emission and excitation spectra were measured with a PTI QM-1 fluorometer. All processing steps and measurements were carried out in the air.

The excitation spectra of dilute solutions of **1a**, **1b** and **1c** are shown in Figure 1. The excitation spectra were obtained by monitoring the emission band at 480 nm and the spectra shown have been normalized to a constant value at 468 nm. The excitation bands near 468 nm are due to the anthracene core as revealed by the absorption spectra of the dendrimers **1a-c** and **2a-b** (the anthracene core exhibits two absorption bands at 446 and 471 nm). The excitation bands at 313 nm are due to both phenylacetylene segments and the anthracene core. The relative intensity of the excitation band at 313 nm increases smoothly with dendrimer generation. This result indicates that there is increasing number of energy collection sites (phenylacetylene segments) in the macromolecule, which are coupled to the anthracene core in an efficient way, even in the highest generation dendrimer.

The current-voltage characteristics of the diodes based on **1c** and **2b** in the forward bias (positive voltage on ITO electrode) are shown in Figure 2. Using dendrimer **1c** as the emitter and Mg/Ag as the electron injecting electrode, the current is observed to increase significantly above 10 V, which is identical to the threshold of electroluminescence. In contrast, no significant current or electroluminescence is observed when an Al electrode is used for the device. This can be rationalized in terms of the difference in the work functions of the metals ($\Phi_{Mg} = 3.66$ V and $\Phi_{Al} = 4.28$ V), a higher work function providing a higher barrier for electron injection. A more efficient

electron injection from the Mg electrode into the LUMO of **1c** contributes to this dramatic improvement. A similar increase in EL efficiency of PPV polymers has been reported by Hsieh and coworkers.[14] The I-V characteristics of device from **2b** show an onset voltage of 3 V with either Mg/Ag or Al contacts. This result indicates that hole injection is improved by the introduction of triphenylamine groups in the periphery of the dendrimer, with the effect that current passage is now limited by hole injection at the indium tin oxide electrode. It should be noted that the large difference in turn-on voltage between devices based on **1c** and **2b** might also be due to the film thickness and different charge injection processes. This would explain why both Mg/Ag and Al can be used as the electron injecting electrode but not affect the onset voltage and current density. Furthermore, incorporation of triphenylamine as the hole-trapping group in the LED from **2b** favorably increases the current density (10x) as compared with the LED from **1c**, and thus accounts for lower turn-on voltage in the former device (*vide infra*). The LEDs based on **1b** and **2a** have I-V characteristic similar to devices from **1c** and **2b**, respectively. Nevertheless, the LEDs from **1b** and **2a** exhibit much poor stability and weaker EL intensity than those from **1c** and **2b**. This is possibly due to crystallization of the films of **1b** and **2a**, initiated by heat produced in the device.

The photoluminescent (PL) and electroluminescent (EL) spectra of films of **1c** and **2b** are shown in Figure 3. Both dendrimers show two major photoluminescence bands at 480 and 510 nm in solution, while a broad, structureless emission band at 600 nm is observed in the films. The red shift and structureless features of the fluorescence spectrum observed in the film is probably due to solid state aggregation of dendrimers.[15] Dilution experiments in solid films suggest that this aggregation is not caused by interactions between the monodendron and the anthracene chromophore. The EL spectra are similar to the PL spectra, suggesting that the luminescence is produced by recombination of holes and electrons in the anthracene core. However, a blue shift (~ 50 nm) is observed in the EL spectra compared to the PL spectra. This phenomenon has

been observed in other organic materials including poly(p-phenylene),[16] poly(3-cyclohexylthiophene),[17] and poly(p-phenylenevinylene).[18,19] Since absorption by the dendrimer in the region (> 500 nm) is insignificant, the shift cannot be attributed to self-absorption. One possibility is that EL takes place in a narrow zone at the heterojunction of dendrimer and electrode, where the electronic structure may not be the same as that in the bulk material. Only modest EL intensities are observed for LEDs from **1c** and **2b**, in part because luminescent intensities are greatly diminished by the solid state aggregation and quenching. Although LEDs from **1c** and **2b** both show the same EL spectra, it should be stressed that LEDs based on **2b** have enhanced intensity because of the increased current density.

In conclusion, we have shown that novel electroluminescent diodes with single-organic-layer configuration are possible using structurally well-defined dendritic materials. High quality amorphous films can be prepared by conventional spin coating. These results demonstrate that a modular approach to the design and construction of electroluminescent materials may provide a systematic approach to alter the active layer of organic LEDs. Efforts are underway to optimize the dendrimer segment to improve device performance.

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Figure captions

Figure 1.   Excitation spectra of (a) **1a**, (b) **1b**, and (c) **1c** in THF (1 x 10-6M). The spectra were obtained by monitoring emission at 480 nm. The excitation bands at 468 nm for all three spectra have been normalized to the same intensity. The inset shows the relative intensity of the excitation band at 313 nm for dendrimers **1a, 1b**, and **1c**.

Figure 2.   (a) Typical current-voltage characteristics of a device from **1c** with Mg/Ag (■) and Al (o) electron injecting electrodes. (b) Typical current-voltage characteristics of a device from **2b** with Mg/Ag (■) and Al (o) electron injecting electrodes.

Figure 3.   Photoluminescent spectra (solution and film) and electroluminescent spectra of (a) **1c** and (b) **2b**. PL: excitation wavelength, 450 nm. EL: drive voltages for LEDs based on **1c** and **2b** (both with Mg/Ag electron injecting electrodes) are 25 V and 12 V, respectively.
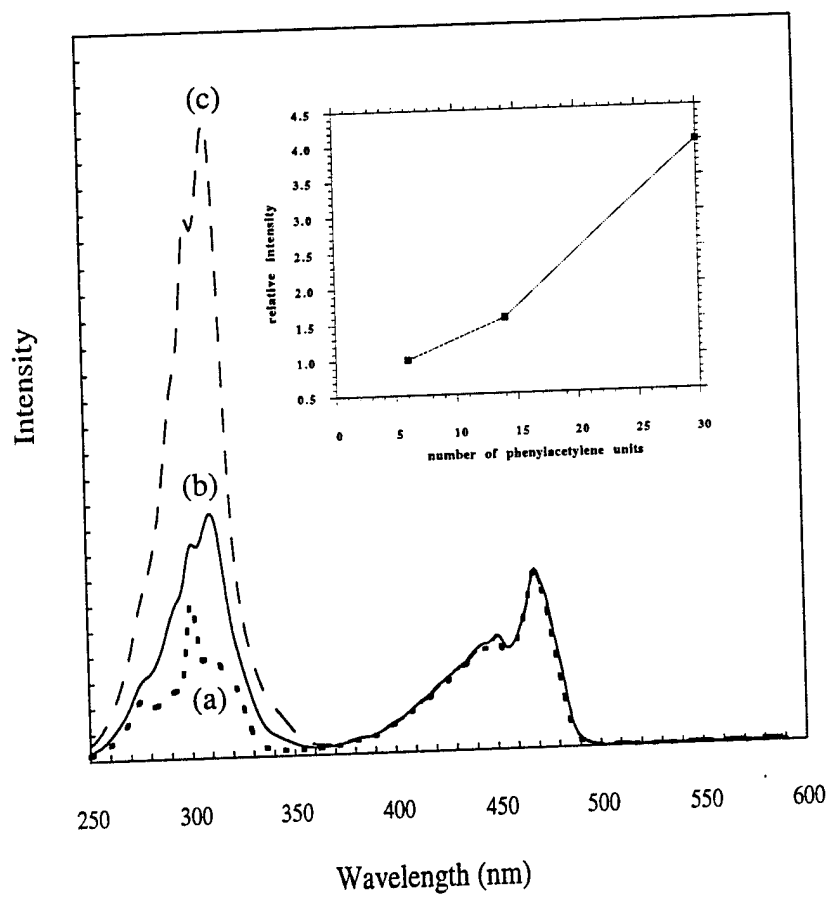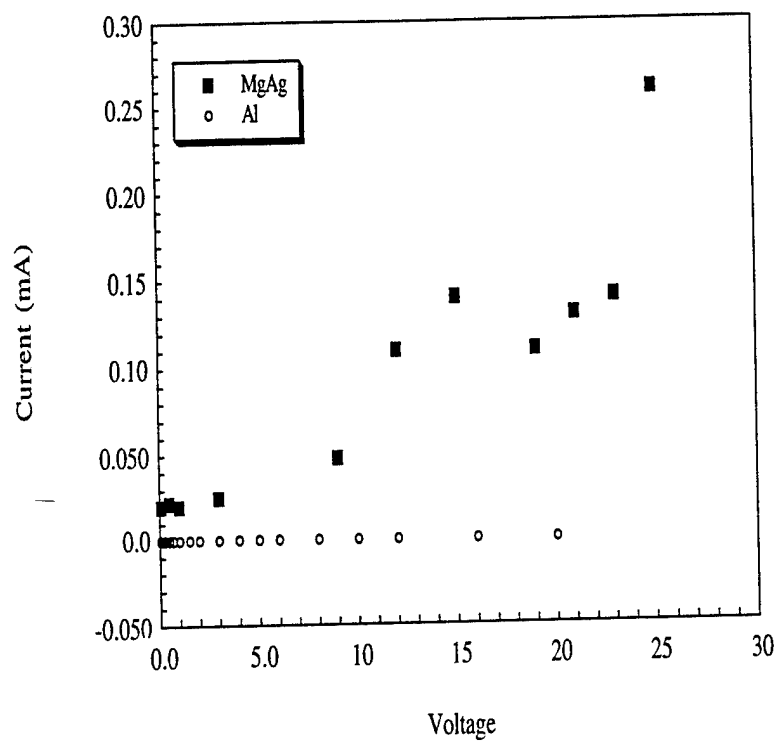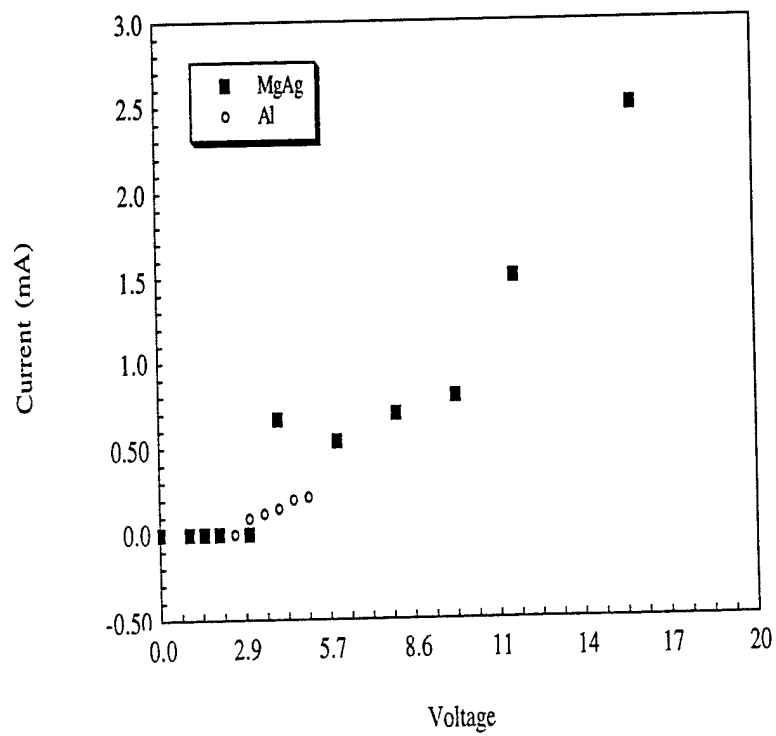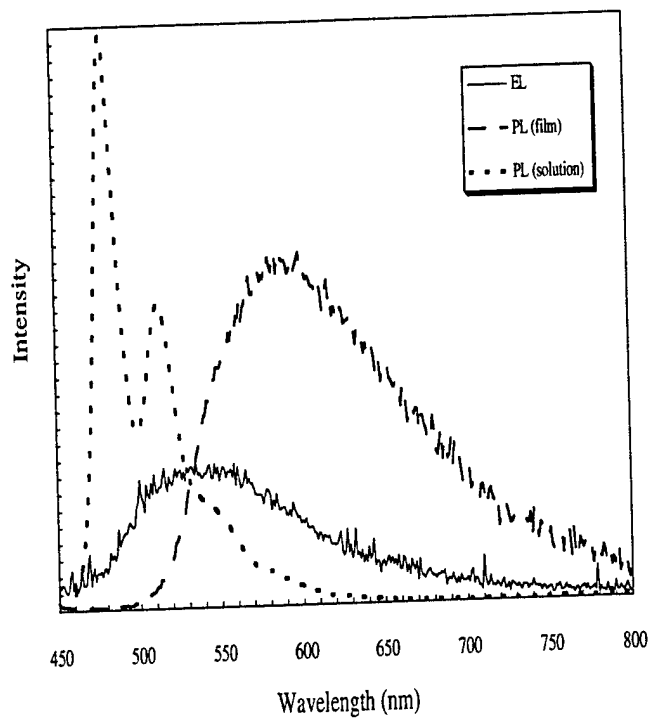
Fig. 1

Fig. 2-a
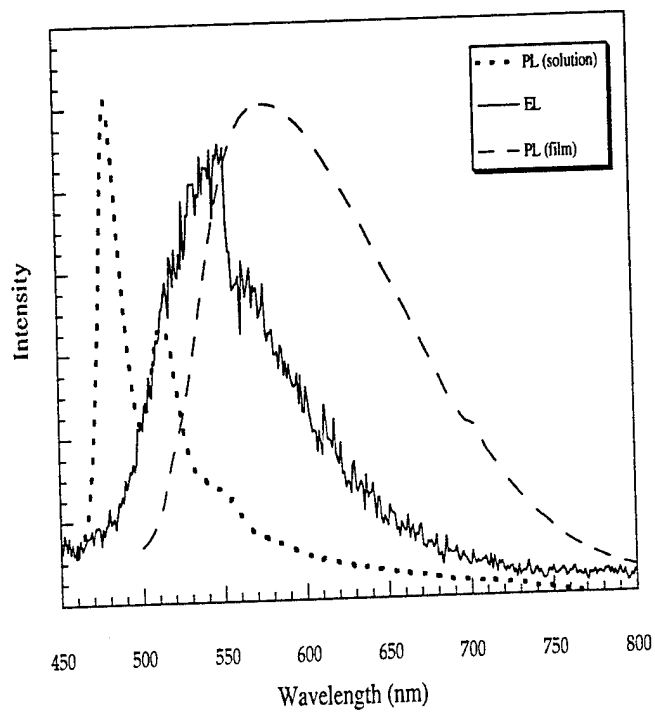

Fig. 2-b

Fig. 3-a

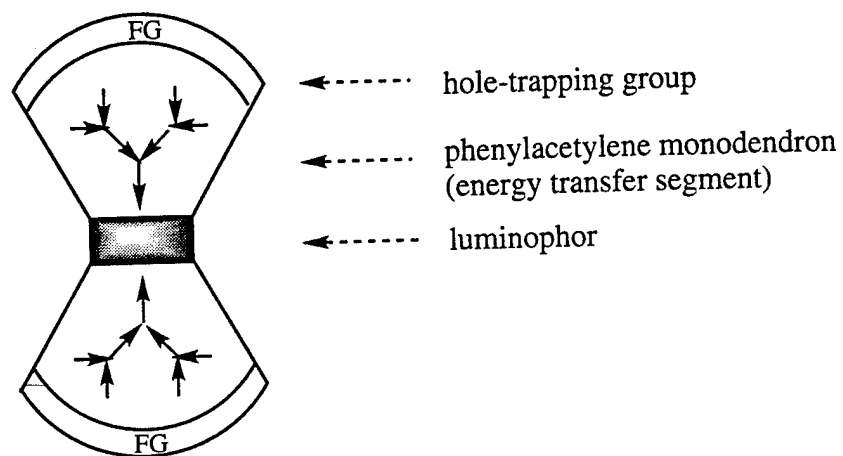Fig. 3-b

Scheme 1. Modular design of electroluminescent materials based on dendritic macromolecules.

FG

FG

◄ - - - - - hole-trapping group

◄ - - - - - phenylacetylene monodendron
(energy transfer segment)

◄ - - - - - luminophor

Scheme 2. Chemical structures of luminescent phenylacetylene dendrimers.
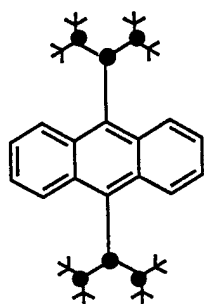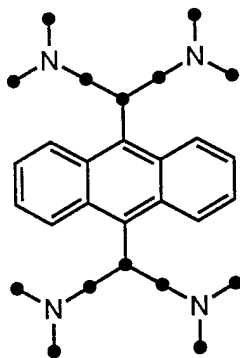
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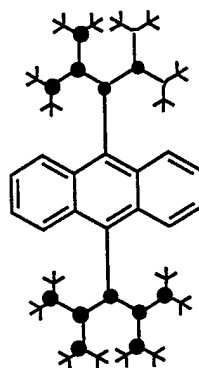
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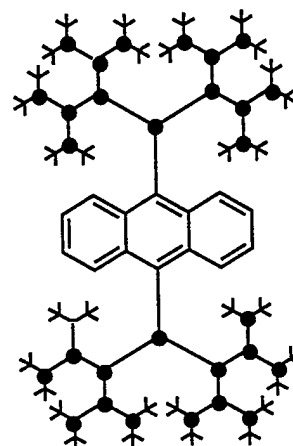
1c

2a

2b
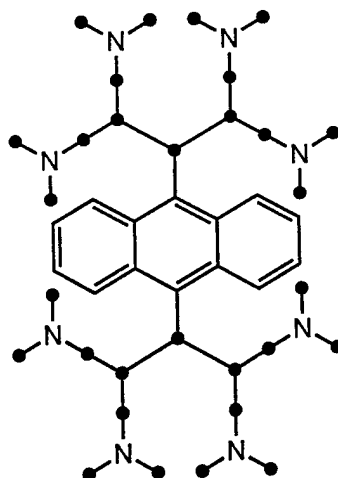
Structure key:

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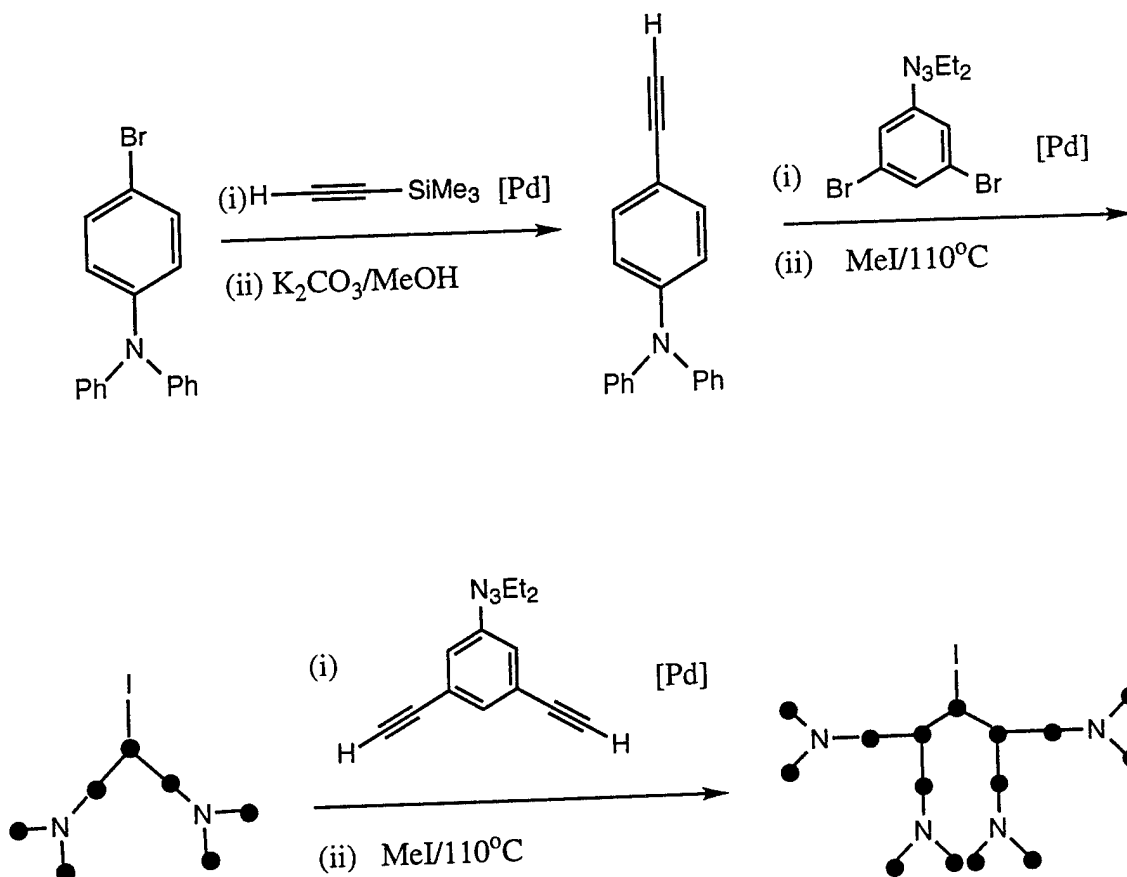
—— : ethynyl

• : phenylene

N—• : N⬡

Electroluminescent Diodes from a Single-Component Emitting Layer of Dendritic Macromolecules

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Supplemental materials

Scheme 3. Synthesis of triphenylamine-modified phenylacetylene monodendrons.

4-Ethynyltriphenylamine was prepared from 4-bromotriphenylamine and (trimethylsilyl)acetylene using the general coupling procedure,[5b] and the product, (4-trimethylsilyl)triphenylamine was hydrolyzed with K_2CO_3 in $CH_2Cl_2/MeOH$ (1/10) to give the title compound. Yield, 75 %. ^1H NMR ($CDCl_3$) δ 7.40 ~ 7.25 (m, 6H), 7.20 ~ 6.96 (m, 8H), 3.05 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 148.38, 147.17, 133.12, 129.48, 125.09, 123.69, 122.12, 114.85, 83.98, 76.33. Anal. Calcd for $C_{20}H_{15}N$: C, 89.19; H, 5.61; found: C, 89.30; H, 5.43.

NW₇-N₃Et₂ was prepared from 4-ethynyltriphenylamine and 3',5'-dibromophenyl-3,3-diethyltriazine using the general coupling procedure.[5b] The product

was purified by flash chromatography eluting with CH_2Cl_2/hexane (2/3). Yield, 75 %. ^1H NMR ($CDCl_3$) δ 7.55 (d, J = 1.2 Hz, 2H), 7.45 (t, J = 1.2 Hz, 1H), 7.41 ~ 7.27 (m, 12H), 7.15 ~ 7.01 (m, 16H), 3.79 (q, J = 7 Hz, 4H), 1.30 (t, J = 7 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 151.23, 147.93, 147.22, 132.62, 130.77, 129.43, 125.00, 124.16, 123.56, 123.19, 122.33, 116.13, 89.63, 88.45. Anal. Calcd for $C_{50}H_{41}N_5$: C, 84.36; H, 5.80; found: C, 84.20; H, 5.60. MS (FAB): calcd, 711.9; found, 712.4.

NW_7-I was prepared by deprotection of NW_7-N_3Et_2 with MeI using the general deprotection procedure,[5b] and the product was purified by flash chromatography eluting with CH_2Cl_2/hexane (15/85). Yield, 88 %. ^1H NMR ($CDCl_3$) δ 7.79 (d, J = 1.1 Hz, 2H), 7.60 (t, J = 1.1 Hz, 1H), 7.38 ~ 7.21 (m, 12H), 7.15 ~ 7.00 (m, 16H). ^{13}C NMR ($CDCl_3$) δ 148.34, 147.07, 139.10, 133.33, 132.66, 129.46, 125.63, 125.10, 123.75, 121.99, 115.15, 93.21, 91.64, 86.37. Anal. Calcd for $C_{46}H_{31}N_2I$: C, 74.80; H, 4.23; found: C, 75.21; H, 4.47.

NW_{15}-N_3Et_2 was prepared from NW_7-I and 3',5'-diethynylphenyl-3,3-diethyltriazine using the general coupling procedure.[5b] The product was purified by flash chromatography eluting with CH_2Cl_2/hexane (3/7). Yield, 61 %. ^1H NMR ($CDCl_3$) δ 7.65 (s, 6H), 7.50 (s, 1H), 7.43 ~ 7.29 (m, 26H), 7.18 ~ 7.04 (m, 32H), 3.83 (q, J = 11 Hz, 4H), 1.31 (br, 6H). ^{13}C NMR ($CDCl_3$) δ 151.38, 148.22, 147.16, 133.86, 133.65, 132.71, 131.04, 129.48, 125.12, 124.38, 124.05, 123.87, 123.70, 123.57, 122.16, 115.55, 90.94, 90.00, 88.14, 87.31. MS (FAB): calcd for $C_{106}H_{75}N_7$, 1446.8; found, 1446.6.

NW_{15}-I was prepared by deprotection of NW_{15}-N_3Et_2 with MeI using the general deprotection procedure.[5b] The product was purified by flash chromatography eluting with CH_2Cl_2/hexane (3/7). Yield, 95 %. ^1H NMR ($CDCl_3$) δ 7.87 (s, 2H), 7.70 ~ 7.61 (s, 7H), 7.45 ~ 7.25 (m, 24H), 7.20 ~ 7.00 (m, 32H). ^{13}C NMR ($CDCl_3$) δ 148.26, 147.12, 140.00, 134.20, 133.59, 132.72, 129.49, 125.15, 125.03, 124.99, 124.51, 123.73, 123.16, 122.10, 115.39, 93.36, 91.16, 90.05, 87.78, 87.14. MS (laser desorption): calcd for $C_{102}H_{65}N_4I$, 1473.6; found, 1475.3.

1a was prepared from 9,10-bis(trimethylsilylethynyl)-anthracene and W$_3$-I according to the coupling procedure (see text), and purified by flash chromatography eluting with CH$_2$Cl$_2$/hexane (95/5). Yield, 70 %. ^{1}H NMR (CDCl$_3$) δ 8.75 ~ 8.7 (m, 4H), 7.92 ~ 7.9 (m, 4H), 7.82 ~ 7.78 (m, 2H), 7.75 ~ 7.67 (m, 4H), 7.45 (s, 12H), 1.36 (s, 72H). ^{13}C NMR (CDCl$_3$) δ 150.95, 134.55, 133.77, 132.16, 127.24, 127.09, 126.00, 124.50, 123.98, 123.18, 121.69, 118.33, 101.09, 91.92, 87.41, 86.63, 34.87, 31.35. MS (FAB): calcd for C$_{94}$H$_{98}$, 1227.03; found, 1227.3. Anal. Calcd for C$_{94}$H$_{98}$: C, 92.01; H, 7.99; found: C, 91.21; H, 7.88.

1b was prepared from 9,10-bis(trimethylsilylethynyl)-anthracene and W$_7$-I according to the coupling procedure (see text), and purified by flash chromatography eluting with CH$_2$Cl$_2$/hexane (88/12). Yield, 60 %. ^{1}H NMR (CDCl$_3$) δ 8.75 ~ 8.7 (m, 4H), 7.92 ~ 7.9 (m, 4H), 7.8 ~ 7.7 (m, 18H), 7.45 ~ 7.4 (m, 24H), 1.36 (s, 144H). ^{13}C NMR (CDCl$_3$) δ 150.92, 134.52, 134.33, 133.95, 132.11, 127.20, 125.98, 124.38, 124.26, 124.01, 123.31, 123.15, 121.70, 100.77, 91.82, 89.50, 88.57, 87.82, 86.5734.85, 31.33. MS (laser desorption): calcd for C$_{190}$H$_{194}$, 2476.09; found, 2477.8. Anal. Calcd for C$_{190}$H$_{194}$: C, 92.16; H, 7.84; found: C, 91.78; H, 8.21.

1c was prepared from 9,10-bis(trimethylsilylethynyl)-anthracene and W$_{15}$-I according to the coupling procedure (see text), and purified by flash chromatography eluting with CH$_2$Cl$_2$/hexane (85/15). Yield, 60 %. ^{1}H NMR (CDCl$_3$) δ 8.75 ~ 8.7 (m, 4H), 7.96 ~7.94 (m, 4H), 7.8 ~ 7.6 (m, 42H), 7.35 ~ 7.45 (m, 48H), 1.37 (s, 288H). ^{13}C NMR (CDCl$_3$) δ 150.91, 134.49, 134.43, 133.92, 132.20, 127.48, 127.22, 126.02, 124.36, 123.90, 123.62, 123.30, 123.14, 121.68, 91.80, 91.33, 89.42, 89.12, 88.89, 88.47, 86.55, 34.82, 31.32. MS (laser desorption): calcd for C$_{382}$H$_{386}$, 4974.2; found, 4989.0. Anal. Calcd for C$_{382}$H$_{386}$: C, 92.23; H, 7.77; found: C, 91.46; H, 7.81.

2a was prepared from NW$_7$-I and 9,10-bis(trimethylsilylethynyl)-anthracene using the coupling procedure (see text), and the product was purified by flash chromatography eluting with CH$_2$Cl$_2$/hexane (1/3). Yield, 35 %. ^{1}H NMR (CDCl$_3$) δ

8.68 (m, 4H), 7.86 (s,4H), 7.70 (m, 6H), 7.43 ~ 7.20 (m, 26H), 7.20 ~ 6.90 (m, 32H). MS (FAB): calcd. for $C_{110}H_{70}N_4$, 1447.8; found, 1447.7.

2b was prepared from NW_{15}-I and 9,10-bis(trimethylsilylethynyl)-anthracene using the coupling procedure (see text), and the product was purified by flash chromatography eluting with CH_2Cl_2/hexane (7/5). Yield, 59 %. ^{1}H NMR (CDCl$_3$) δ 8.70 ~ 8.60 (m, 4H), 7.91 (br, 4H), 7.75 (br, 2H), 7.70 ~ 7.60 (m, 12H), 7.42 ~ 7.20 (m, 48H), 7.15 ~ 6.90 (m, 68H). ^{13}C NMR (CDCl$_3$) δ 148.18, 147.13, 134.21, 133.64, 132.71, 132.02, 129.45, 127.00, 125.11, 124.45, 124.21, 123.95, 123.67, 123.33, 122.11, 115.52, 91.04, 89.59, 88.72, 88.00, 87.26. MS (laser desorption): calcd for $C_{222}H_{138}N_8$, 2917.6; found, 2918.3.

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